

Pressure induced phase transition and amorphization of Na₃ONO₂

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The high pressure behavior of Na₃ONO₂ has been investigated by Raman spectroscopy and angle-dispersive X-ray diffraction from synchrotron radiation by using the diamond anvil cell technique. Pressure induced phase transitions and finally amorphization are observed. Starting from cubic symmetry at ambient conditions Na₃ONO₂ transforms to a rhombohedral high pressure phase at 0.7 GPa. Beyond 14.1 GPa, the crystalline structure destabilizes and amorphous state is achieved.

1. Introduction

Na₃NO₃, known since 1937, was first regarded as sodium orthonitrite.¹ In 1977, using single crystal X-ray diffraction, the true nature of the compound was discovered to be sodium oxide nitrite, Na₃O(NO₂), with a cubic anti-perovskite type structure.^{2–4} The NO₂[−] ion, disordered at room temperature, occupies the cuboctahedral interstices formed by the 12 Na⁺ ions of the (Na₃O)⁺ framework. Recent neutron scattering studies⁵ have shown that, upon cooling, Na₃ONO₂ undergoes crystallographic phase transitions from a cubic (space group *Pm3̄m*) to a tetragonal M-Na₃ONO₂ (space group *I4/mcm*) structure at 240 K, then to a tetragonal T-Na₃ONO₂ (space group *P4/mbm*) structure at 178 K, and to a tetragonal TT-Na₃ONO₂ (space group *P4̄2₁m*) structure around 68 K, due to one discontinuous and two continuous ordering processes of the nitrate ion. The high pressure behavior of Na₃ONO₂, particularly with regard to the possibility of pressure induced formation of the still unknown NO₃^{3−} ion, has not been examined. This Communication reports the results of X-ray powder diffraction studies of Na₃ONO₂ at high pressures up to 18 GPa at room temperature and 573 K, respectively.

2. Experimental

Na₃ONO₂ was prepared by the solid state reaction of sodium oxide (Na₂O) and sodium nitrite (NaNO₂) as previously described.⁴ The crystal structure has been determined at ambient conditions using X-ray and neutron diffraction data.^{2–5} The high pressure experiments were carried out in a diamond anvil cell (DAC) apparatus. The sample was loaded in a hole of T301 steel gasket in a glove box and no pressure transmitting medium was used due to the severely hygroscopic character of the sample. The pressure was calibrated by the ruby luminescence method.⁶ The angle-dispersive X-ray powder diffraction experiments ($\lambda = 0.4154 \text{ \AA}$) in a DAC were performed at the beam line ID9 of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Diffraction patterns were

recorded on an image plate and then integrated by using the program FIT2D.⁷ Raman spectra were collected at room temperature by a Jobin-Yvon LabRAM laser microscope Raman system using a CCD detector with excitation line 632.8 nm (He–Ne laser).

3. Results and discussion

The change of Raman spectra of the sample with increasing pressure is shown in Fig. 1. At ambient condition, two Raman modes, the δ mode and the ν_{as} mode of the NO₂[−] ion,³ are observed. Both Raman modes show a trend to higher frequencies as a function of pressure. For the δ mode, the ratio of $d\omega/dP$ is estimated as $2.13 \text{ cm}^{-1} \text{ GPa}^{-1}$. The ν_{as} mode is located near the Raman peak of diamond, which was used as the high pressure cell anvils, and overlaps with the diamond peak during the compressing process after 10.3 GPa and the $d\omega/dP$ is

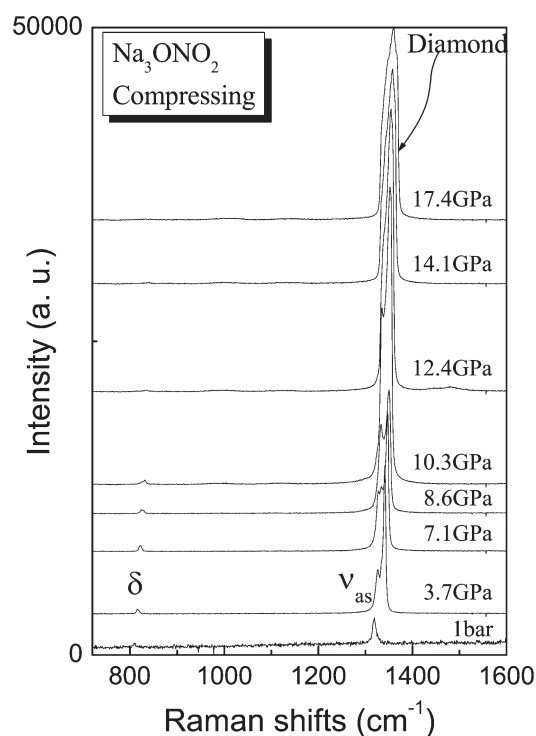


Fig. 1 Raman spectra of Na₃ONO₂ upon compression.

estimated as $1.44 \text{ cm}^{-1} \text{ GPa}^{-1}$. This enables us to determine the mode Grüneisen parameter $\gamma_G = -\frac{\partial \ln \omega}{\partial \ln V}$, which is evaluated at zero pressure as $\gamma_G = \frac{K_0}{\omega_0} \frac{\partial \omega}{\partial P}$. The zero pressure bulk modulus, K_0 , is estimated as 47.5 GPa for the high pressure phase which is obtained from X-ray diffraction analysis (see later). Then γ_G are calculated as 0.125 for the δ mode and 0.052 for the ν_{as} mode, respectively.

The intensity of the δ mode decreases with increasing pressure, it is observed up to 12.4 GPa, and it completely disappears at 14.1 GPa. None of the Raman peaks recover and no Raman active peak, *i.e.* neither the Raman modes of NO_2^- nor the hypothetical NO_3^{3-} , which are possible reaction products, could be observed during the decompressing process from 17.4 GPa to 0.2 GPa. These results indicate that bonds between N–O in the sample are cleaved above a pressure of 14.1 GPa, and imply that the pressure induced structural conversion is an irreversible process.

Fig. 2 shows the typical XRD patterns of the sample under various pressures during the compressing processes. Using the program GSAS,⁸ the Rietveld refinements were carried out for all of the diffraction patterns. The 4th profile function in GSAS was adopted since this function uses the microstrain broadening description⁹ and is more suited to high pressure conditions than other profile functions in GSAS. The results reveal that Na_3ONO_2 loses its cubic (space group $Pm\bar{3}m$) symmetry and transforms to a rhombohedral (space group $R\bar{3}m$) high pressure phase (R- Na_3ONO_2) at about 0.7 GPa. The main structural feature of the anti-perovskite structure remains unchanged during the pressure induced phase transition process due to the similarities of the diffraction patterns to the cubic structure. Fig. 3 shows a typical refinement result of the powder pattern at 1.3 GPa during compression, in which the background of diffraction pattern is removed first and the refinement converged to $R_p = 14.3\%$, $R_{\text{wp}} = 18.7\%$.

Fig. 4 shows the lattice parameters of R- Na_3ONO_2 as a function of pressure. As a result of the pressure induced distortion the perfect cubic framework of $(\text{Na}_3\text{O})^+$ transforms to a rhombohedral symmetry, the unit cell angle changes from 90° at ambient conditions to 90.92° at 0.7 GPa, and then gradually to 94.68° at 10.1 GPa. When the pressure is increased up to 11.9 GPa, the ratio between intensities of reflections and background in the diffraction pattern decreases. After 14.5 GPa the crystalline structure of Na_3ONO_2 is destabilized and an X-ray diffraction amorphous state is achieved. The sample remains amorphous when the pressure was increased up to 18 GPa, as it does upon decompressing down to 0.5 GPa. This behavior of pressure induced amorphization is in agreement

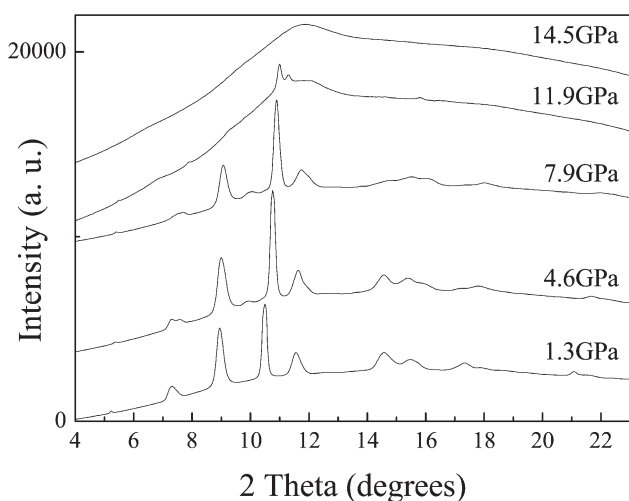


Fig. 2 XRD patterns of Na_3ONO_2 during compression.

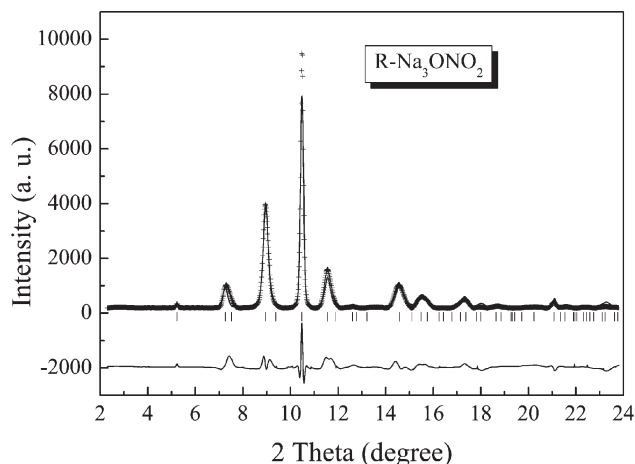


Fig. 3 Observed, calculated, and difference XRD profile of R- Na_3ONO_2 at 1.3 GPa.

with the high pressure Raman results. The reason for the change from crystalline state to an amorphous one seems to be a proceeding decomposition of the sample. This decomposition proceeds *via* cleavage of N–O bonds instead of structural separation into the normal decomposition products Na_2O and NaNO_2 which is shown by the missing reflections in the X-ray diffraction patterns as well as the lack of any NO_2^- ν or δ modes in the Raman spectra of the sample after it was compressed with more than 14.5 GPa. As another result from the lack of Raman modes we can exclude the desired formation of the hypothetical NO_3^{3-} ion. The product, possibly a mixture of different phases, does not crystallize again during decompressing and may be inhibited by its topological features because of the lack of activation energy which is necessary for the rearrangement in the solid state.

The pressure induced amorphization has attracted intensive attention from a fundamental viewpoint over the last two decades.^{10–13} Amorphous solids, which have no long-range order and are frozen into a particular structural arrangement, are metastable with respect to crystalline phases. The different mechanisms of pressure induced amorphization were proposed pertaining to special compounds. One mechanism suggests a negative pressure dependence of the melting temperature, thus the extension of the melting curve would pass through the amorphization pressure at room temperature, as observed in ice-I, SiO_2 , and $\text{Ca}(\text{OH})_2$ cases of pressure induced amorphization.^{10–12} For Na_3ONO_2 , a slow decomposition instead of melting occurs on heating up to 623 K at normal pressure, this

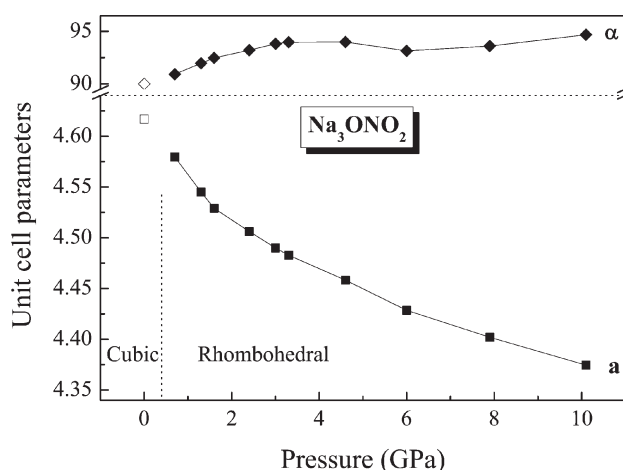


Fig. 4 The lattice parameters of Na_3ONO_2 as a function of pressure, in which a is in Angstrom and α in degree.

encouraged us to perform high temperature high pressure experiments in order to check the possible negative pressure dependence of the decomposition temperature.

Using an internal heating DAC device, the high pressure angle-dispersive X-ray powder diffraction experiments at a temperature of 573 K were carried out to compare with the room temperature results. Firstly we increased the pressure up to 5 GPa, then heated to 573 K and remained at this temperature, then increased the pressure up to 15 GPa. The impurity peaks of Na₂O and NaNO₂, which are products of decomposition at ambient condition, are observed together with those of Na₃ONO₂ in the XRD patterns measured under a pressure range of 5–12 GPa. Compared to room pressure where the decomposition temperature is 623 K, the relative lower decomposition temperature under higher pressure conditions reveals the characteristic of pressure induced structural destabilization of Na₃ONO₂. The X-ray reflections disappear upon compression beyond 13 GPa at 573 K, this pressure is a little lower than the amorphization pressure of 14.5 GPa at room temperature. Therefore the negative pressure dependence of decomposition and amorphization temperature was observed.

In addition to some general interest in the high pressure behavior of Na₃ONO₂, the orientational disorder of nitrite ion inside the sodium oxide framework is of special interest. The orientational disorder is expected to be reduced under high pressure while the sodium oxide framework transforms from cubic symmetry to the lower rhombohedral symmetric structure, then it has lost its translational symmetry in the amorphous state. However, the diffraction methods could not really distinguish dynamic disorder phenomena due to the measured patterns being averaged over space and time. The relative poor quality of the high pressure diffraction data, due to stress distribution in the high pressure cell without pressure transmitting medium as well as strong preferred orientation phenomena of the sample, hampered us from obtaining clear information on the evolution of orientational disorder of NO₂[−] under pressure. Therefore the change of the orientational disorder, if present, in the pressure induced decomposition remains unclear. Very recently, solid state nuclear magnetic resonance techniques have been used to study the NO₂[−] disorder phase transition behavior change upon cooling,¹⁴ and this technique may be applied to disclose the corresponding orientational disorder behavior for the high pressure phase in the future.

The behavior change of the relative unit cell volume of R-Na₃ONO₂ with pressure is shown in Fig. 5. The equation of state of R-Na₃ONO₂ could be fitted into the second order Birch equation of state, in which the pressure derivative of the bulk modulus K_0' remains as 4.¹⁵ The zero pressure bulk modulus (K_0) is estimated as 47.5 GPa. It indicates that R-Na₃ONO₂ is a soft high pressure phase, which could work well as a pressure transmitting medium itself in DAC during high pressure experiments.

4. Conclusion

In summary, Na₃ONO₂ has been investigated by *in situ* high pressure angle-dispersive X-ray diffraction from synchrotron radiation and Raman spectroscopy. A phase transition from cubic symmetry at ambient conditions to a rhombohedral

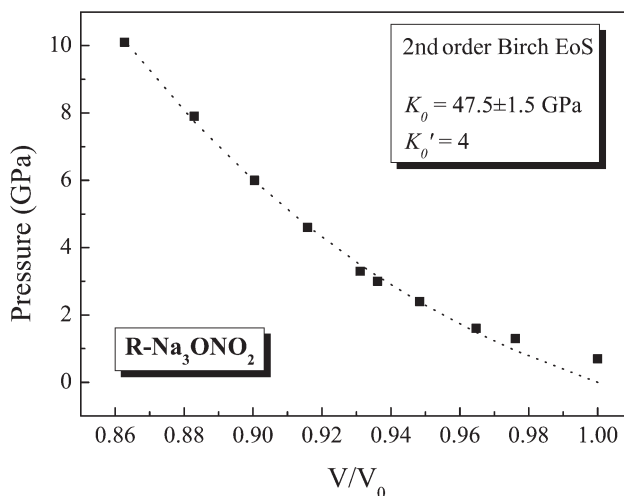


Fig. 5 Pressure dependence of the relative unit cell volume of R-Na₃ONO₂ with increasing pressure (dotted line fitted by the 2nd order Birch EoS).

phase at a pressure of around 0.7 GPa is observed. Beyond 14.1 GPa, the crystalline structure destabilizes and an amorphous state is achieved. The negative pressure dependence of the decomposition temperature of the sample reveals the mechanism of the pressure induced amorphization.

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